



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of : Confirmation No. 2705
Hiroyuki FUJIMURA et al. : Attorney Docket No. 2003_1008A
Serial No. 10/623,159 : Group Art Unit 1742
Filed July 21, 2003 : Examiner Hany D. Wilkins, III
METHOD AND APPARATUS FOR : Mail Stop: AF
PRODUCING HIGH-PURITY HYDROGEN

DECLARATION UNDER 37 C.F.R. § 1.132

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, Hiroshi Yokota, the undersigned, a citizen of Japan, residing at 18-1-1022 Shimokurata-machi Totuka-ku Yokohama-shi 244-0815 Japan, do hereby declare:

1. That I am an employee of the Ebara Corporation and a manager of the Material Laboratory.
2. That I graduated from the University of Tokyo on March 31 1979 with a degree in Metallurgy and received a doctoral degree in engineering from the University of Tokyo at 1992.
3. That I have been employed as a engineer and a researcher at Ebara Corporation from 1979 to the present.

4. That under my control and direction experiments were conducted in order to study the difference in carbon deposition in the process of the present invention and that of the prior art process, which employs methane as the reducing gas.

The particulars and results of the experiments are set forth below. The data is presented in Exhibit I and Graphs 1-4, which are attached hereto.

Graph 3 shows a change in temperature of free energy of formation "AG" of carbon deposition reaction from methane ($\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$) and carbon deposition reaction from CO ($2\text{CO} \rightarrow \text{C} + \text{CO}_2$ or $\text{CO} + \text{H}_2 \rightarrow \text{C} + \text{H}_2\text{O}$). It can be seen from Graph 4 that, while carbon deposition from methane easily occurs at temperatures of more than 550°C , carbon deposition from CO occurs at temperatures of less than 700°C .

Steam electrolysis is performed at a temperature of about 800°C . At this temperature, carbon deposition from CO does not occur, while carbon deposition from methane does occur. Therefore, the use of a reducing gas, composed mainly of hydrogen and carbon monoxide (CO), can avoid the carbon deposition problem.

As a method of preventing carbon deposition from methane, it has been customary to add steam to methane. The curved line in Graph 4, on the attached sheet, shows results of a thermodynamic calculation of the amount of water (steam/ CH_4) required for preventing carbon deposition. It can be seen from Graph 4 that steam/ CH_4 is around 1 in every region. Particularly, in a temperature region between 700 and 500°C , carbon deposition is apt to occur, and it is thus required to increase steam/ CH_4 .

In the case of mixing methane and steam, a steam-reforming reaction occurs on the electrode. This steam-reforming reaction is an intense endothermic reaction, and thus results in a decrease in temperature. Such a decrease in temperature would cause an increase in overvoltage and a decrease in efficiency. Further, because the temperature approaches the above-mentioned region where carbon deposition is apt to occur, it becomes difficult to maintain a stable operation.

However, in the present invention, supplying of the reducing gas causes a slight exothermal reaction. Accordingly, the temperature can be maintained, and a stable operation can be achieved. Further, use of the reducing gas can greatly lower an electrolytic voltage in the high-temperature steam electrolyzer as much as in the case of using methane. Therefore, use of the reducing gas is economically advantageous in view of it being produced from a low-cost organic material.

An experiment was conducted according to the present invention as follows. Under a temperature of 734°C, steam was supplied into a cylindrical electrolytic cell, and a simulated pyrolysis gas (H_2 : 58.6%, CO: 24.1%, CO_2 : 12.4%, methane: 4.8%) was supplied to the outside of the electrolytic cell. In this state, a voltage was applied between an outside electrode (anode) and an inside electrode (cathode).

The voltage-current curve obtained during the experiment is represented in Graph 1. The following information can be gleaned from Graph 1. When the current was zero, the voltage was -180 mV. As the current increased, the voltage also increased substantially linearly. Thus, it was confirmed that continuous electrolysis was able to be performed stably.

Next, the experiment was conducted using methane instead of the simulated pyrolysis gas. The results of this experiment are also shown in Graph 1. In the case of methane, when the current was zero, the voltage was -360 mV. However, as the current increased, the voltage sharply increased. As a result, a higher voltage was required in comparison with the voltage required in the present invention. This means that more electric power is required when producing the same amount of hydrogen, and that significant unexpected advantages are obtained by using pyrolysis gas instead of methane.

Further, in order to study whether or not carbon was deposited on the electrode as a result of the electrolysis process using methane, an inert gas (N_2) was introduced into the apparatus in order to expel (purge) the methane, and then humidified nitrogen gas ($N_2 + H_2O$) was supplied to the electrode. More specifically, N_2 gas was introduced for about 600 seconds, and then $N_2 + H_2O$ were supplied to the electrode. As a result, as shown in Graph 2, CO and CO_2 were produced from the electrode. This is due to the fact that the carbon gas was deposited on the electrode as a result of electrolysis using methane and that carbon reacted with H_2O to thereby produce CO and CO_2 .

With reference to Graph 3, it can be seen that carbon deposition from methane occurs at temperatures of more than $550^\circ C$, while carbon deposition from CO occurs at temperatures of less than $700^\circ C$. Since electrolysis is performed at a temperature of approximately $800^\circ C$, carbon deposition from CO will not occur at this temperature. Therefore, based on the results of the experiments, it was discovered that the use of a reducing gas composed mainly of hydrogen and carbon monoxide (CO) can avoid the carbon deposition problem.

I further declare that all statements made herein of my own knowledge are true and all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent issuing thereon.

Date: June 26, 2007

Hiroshi Yokota
Hiroshi Yokota